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असाधारण

EXTRAORDINARY

भाग II—खण्ड 3—उप-खण्ड (i)

PART II—Section 3—Sub-section (i)

प्राधिकार से प्रकाशित

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इस भाग में भिन्न पृष्ठ संख्या दी जाती है जिससे कि यह अलग संकलन के रूप में रखा जा सके।

Separate paging is given to this Part in order that it may be filed as a separate compilation.

MINISTRY OF FOOD, AGRICULTURE, COMMUNITY DEVELOPMENT AND COOPERATION

(Department of Agriculture)

New Delhi, the 23rd January, 1970

**G.S.R. 217**—In exercise of the powers conferred by section 3 of the Essential Commodities Act, 1955 (10 of 1955), the Central Government hereby makes the following Order further to amend the Fertiliser (Control) Order, 1957, namely:—

- (1) This Order may be called the Fertiliser (Control) Amendment Order, 1970.
- (2) In clause 2 of the Fertiliser (Control) Order, 1957 (hereinafter referred to as the said Order),—
  - (i) in items (d) and (k), for the words “the Schedule”, the word and figure “Schedule I” shall be substituted;
- (3) For clause 7 of the said Order, the following clause shall be substituted, namely:—
 

“7. Grant and refusal of registration

The Registering Authority shall grant a certificate of registration in Form ‘B’ within thirty days of the receipt of application, to any person who applies for it under clause 6, unless such

person had been convicted for any offence under the Essential Commodities Act, 1955 (10 of 1955) or any Order made thereunder within three years preceding the date of application."

(4) In sub-clause (1) of clause 13 of the said order, in item (b),—

- (i) in sub-item (v), the word "or", occurring at the end shall be omitted;
- (ii) in sub-item (vi), the word "or" shall be added at the end;
- (iii) after sub-item (vi), the following sub-item shall be inserted, namely:—

"(vii) any fertiliser without exhibiting the minimum guaranteed percentage by weight of plant nutrients."

(5) After clause 13A of the said Order, the following clause shall be inserted, namely:—

"13B. *Disposal of non-standard fertilisers.*—Notwithstanding anything contained in the Order a person may sell, offer for sale, stock, or exhibit for sale or distribute, any fertiliser not conforming to the prescribed standard (hereinafter in this Order referred to as non-standard fertiliser) subject to the conditions that—

- (a) the container of such non-standard fertiliser is conspicuously superscribed with the words "non-standard" and also with the sign "X", both in red colour; and
- (b) an application for the disposal of non-standard fertilisers in Form 'F' is submitted to the registering authority to grant certificate of registration for sale of such fertilisers and a certificate of authorisation with regard to their disposal and price is obtained in Form 'G'.

Provided that the price per unit of the non-standard fertiliser shall be fixed by such registering authority after satisfying itself that the sample taken is a representative one, and after considering the nutrient content in the sample determined on the basis of a chemical analysis of the non-standard fertiliser."

(6) In clause 14 of the said order,—

- (i) in sub-clause (1), after item (b), the following provisos shall be inserted, namely:—

"Provided that where fertiliser manufactured in India are packed in bags stitched in hand, such bags shall bear lead seals, so that the contents thereof cannot be tampered with without breaking the seals;

Provided further that lead sealing shall not be necessary if such bags are machine-stitched in such a manner that contents thereof cannot be tampered with without a visible break in the stitching."

- (ii) after sub-clause (1), the following sub-clause shall be inserted, namely:—

"1A. Notwithstanding anything contained in sub-clause (1), a manufacturer may sell the fertilisers manufactured by him in bulk to a manufacturer of compound fertilisers, mixtures of fertilisers or special mixtures of fertilisers."

(7) After clause 14 of the said order, the following clause shall be inserted, namely:—

"14A. The State Government may, by notification in the Official Gazette, with effect from the date to be specified therein,—

- (a) authorise Inspectors to draw the samples of fertilisers in accordance with the procedure of drawal of samples as laid down in Schedule II to this order;
- (b) direct that samples drawn by the Inspectors shall be analysed in the laboratory or laboratories of the State according to the methods of analysis laid down in Schedule II to this order."

(8) The existing Schedule to the said order shall be numbered as Schedule I and for Schedule I as so renumbered the following Schedule shall be substituted, namely:—

## SCHEDULE I

[See clause 2(d) &amp; (k)]

*A. Specifications of fertilisers*

Name of the Fertilizer	Specifications	
1. Ammonium Sulphate	(i) Percent by weight maximum . . . . .	1.0
	(ii) Ammoniacal nitrogen percent by weight minimum . . . . .	20.6
	(iii) Free acidity (as $H_2SO_4$ ) per cent by weight maximum . . . . .	0.025
	(0.04 for material obtained from by-product ammonia and by-product gypsum)	
	(iv) Arsenic (as $As_2O_3$ ) per cent by weight maximum .	0.01
2. Ammonium Sulphate Nitrate	(i) Moisture per cent by weight, maximum .	1.0
	(ii) Total ammoniacal and nitrate nitrogen per cent by weight minimum, . . . . .	26.0
	(iii) Ammoniacal nitrogen per cent by weight minimum . . . . .	19.25
	(iv) Free acidity (as $HNO_3$ ), per cent by weight, maximum . . . . .	0.015
	(v) <i>Particle size</i> Product size in the range of —4 + 2 mm. I S sieve	
3. Urea . . . . .	(i) Moisture per cent by weight, maximum . . . . .	1.0
	(ii) Total nitrogen, per cent by weight, (on dry basis), minimum . . . . .	46.0
	(iii) Biuret, per cent by weight maximum . . . . .	1.5
	(iv) <i>Particle size</i> In the form of granule the material shall pass I S sieve 320 and not less than 80 per cent by weight of it shall be retained on I S sieve 100. If in the form of prills, the material shall pass I S sieve 200 and not less than 80 per cent by weight of it shall be retained on I S sieve 100.	
4. Ammonium Chloride .	(i) Moisture per cent by weight maximum . . . . .	2.0
	(ii) Ammoniacal nitrogen per cent by weight . . . . .	25.0
	(iii) Chloride other than ammonium chloride (as NaCl) per cent by weight (on dry basis), maximum, . . . . .	2.0
5. Calcium Ammonium Nitrate	(i) Moisture; per cent by weight maximum] . . . . .	1.0
	(ii) Total ammoniacal and nitrate nitrogen per cent by weight minimum, . . . . .	25.0
	(iii) Ammoniacal nitrogen percent by weight minimum . . . . .	12.5
	(iv) Calcium nitrate per cent by weight maximum . . . . .	0.5
	(v) <i>Particle size</i> The particle size of the material shall be such that the material is completely retained on 1 mm I S sieve and not less than 80 per cent, by weight of it shall pass through 4 mm I S sieve.	

Name of the Fertiliser	Specifications	
6. Superphosphate Single	(i) Moisture per cent by weight maximum . . . . . (ii) Free phosphoric acid (as $P_2O_5$ ) per cent by weight maximum . . . . . (iii) Water soluble phosphates (as $P_2O_5$ ) per cent by weight minimum . . . . .	12.0 4.0 16.0
7. Superphosphate Triple	(i) Moisture per cent by weight maximum . . . . . (ii) Free phosphoric acid (as $P_2O_5$ ) per cent by weight maximum . . . . . (iii) Total phosphates (as $P_2O_5$ ) per cent by weight minimum . . . . . (iv) Water soluble phosphates (as $P_2O_5$ ) per cent by weight minimum . . . . .	12.0 3.0 46.0 42.5
8. Dicalcium phosphate .	(i) Moisture per cent by weight, maximum . . . . . (ii) Neutral ammonium citrate soluble phosphates (as $P_2O_5$ ), per cent by weight minimum . . . . . (iii) Chlorides (as c l), per cent by weight maximum . . . . .	8.0 34.0 1.0
9. Bone-Meal, Raw	(i) Moisture, per cent by weight maximum . . . . . (ii) Acid insoluble matter, per cent by weight maximum . . . . . (iii) Total phosphates (as $P_2O_5$ ) per cent by weight minimum . . . . . (iv) Phosphates (as $P_2O_5$ ) soluble in 2 per cent citric acid solution per cent by weight minimum . . . . . (v) Nitrogen content of water insoluble portion, per cent by weight minimum . . . . . (vi) <i>Sieve Analysis</i> The material shall pass wholly through 2.36 I S sieve of which not more than 30 per cent shall be retained on 850 micron I S sieve.	8.0 12.0 20.0 8.0 3.0
10. Bone-Meal steamed	(i) Free moisture per cent by weight maximum . . . . . (ii) Total phosphates (as $P_2O_5$ ) per cent by weight (on dry basis) minimum . . . . . (iii) Phosphates (as $P_2O_5$ ) soluble in 2 per cent citric acid solution, per cent by weight (on dry basis) minimum . . . . . (iv) <i>Particle size</i> Not less than 90 per cent by weight shall pass through 1.18 mm I S sieve.	7.0 22.0 16.0
11. Potassium chloride (Muriate of Potash)	(i) Moisture per cent by weight maximum . . . . . (ii) Potash content (as $K_2O$ ) percent by weight minimum . . . . . (iii) Sodium (as NaCl) per cent by weight (on dry basis) maximum . . . . .	0.5 58.0 3.0
12. Sulphate of Potash	(i) Moisture per cent by weight maximum . . . . . (ii) Potash content (as $K_2O$ ) per cent by weight minimum . . . . . (iii) Total chlorides (as c l) percent by weight (on dry basis), maximum . . . . .	1.5 48.0 2.5

Name of the Fertiliser	Specifications	
	(iv) Sodium as (NaCl) per cent by weight (on dry basis) maximum . . . . .	2.0
13. Diammonium Phosphate (18-46-0)	(i) Moisture per cent by weight maximum . . . . .	1.0
	(ii) Total nitrogen all in ammoniacal form per cent by weight minimum . . . . .	18.0
	(iii) Total Phosphates (as $P_2O_5$ ) per cent by weight minimum . . . . .	46.0
	(iv) Water soluble phosphates (as $P_2O_5$ ) per cent by weight minimum . . . . .	41.0
14. Diammonium Phosphate (20-48-0)	(i) Moisture per cent by weight maximum . . . . .	1.0
	(ii) Total nitrogen all in ammoniacal form, per cent by weight . . . . .	20.0
	(iii) Total Phosphates (as $P_2O_5$ ) per cent by weight minimum . . . . .	48.0
	(iv) Water soluble phosphates (as $P_2O_5$ ) per cent by weight minimum . . . . .	43.0
15. Ammonium Phosphate Sulphate (16-20-0)	(i) Moisture per cent by weight maximum . . . . .	1.0
	(ii) Total ammoniacal nitrogen per cent by weight, minimum . . . . .	16.0
	(iii) Total phosphates (as $P_2O_5$ ) per cent by weight, minimum . . . . .	20.0
	(iv) Water soluble phosphate (as $P_2O_5$ ) per cent by weight minimum . . . . .	19.5
	(v) <i>Particle size</i> Not less than 99.5 per cent will pass through 2.36 mm IS sieve and not less than 99.7 per cent shall be retained on 500 micron IS sieve. The material passing 18mm IS sieve shall not be more than 25 per cent.	
16. Ammonium Phosphate Sulphate (19.5-19.5-0)	(i) Moisture per cent by weight maximum . . . . .	1.0
	(ii) Ammoniacal nitrogen per cent by weight minimum . . . . .	19.5
	(iii) Phosphates (as $P_2O_5$ ) soluble in neutral ammonium citrate solution, per cent by weight minimum . . . . .	19.5
	(iv) Water soluble phosphates (as $P_2O_5$ ) per cent by weight minimum . . . . .	17.5
17. Ammonium Phosphate Sulphate (20-20-0)	(i) Moisture per cent by weight . . . . .	1.0
	(ii) Ammoniacal nitrogen per cent by weight minimum . . . . .	18.0
	(iii) Nitrogen in the form of urea per cent by weight minimum . . . . .	2.0
	(iv) Phosphates (as $P_2O_5$ ) soluble in neutral ammonium citrate solution per cent by weight minimum . . . . .	20.0

Name of the Fertiliser	Specifications	
	(v) Water soluble phosphates (as $P_2O_5$ ) per cent by weight minimum	17.0
	(vi) <i>Particle size</i> Material shall pass through 3.35 mm IS sieve and shall be retained on 1.0 mm IS sieve	
18. Nitrophosphate . (20-20-0)	(i) Moisture per cent by weight maximum	1.5
	(ii) Total nitrogen per cent by weight, minimum	20.0
	(iii) Neutral ammonium citrate soluble phosphate (as $P_2O_5$ ) per cent by weight minimum	20.0
	(iv) Water soluble phosphates (as $P_2O_5$ ) per cent by weight minimum	5.4
	(v) Calcium nitrate	traces
	(vi) <i>Particle size</i> The particle size of the material shall be such that 90 per cent of the material will be between -4mm and +1mm IS sieve.	
19. Nitro Phosphate with Potash Grade I (18-18-9)	(i) Moisture per cent by weight maximum.	1.5
	(ii) Total nitrogen per cent by weight minimum.	18.0
	(iii) Total phosphates (as $P_2O_5$ ) per cent by weight minimum.	18.0
	(iv) Neutral ammonium citrate soluble by weight minimum.	18.0
	(v) water soluble phosphate per cent by weight minimum.	4.9
	(vi) Water soluble potash (as $K_2O$ ) per cent by weight minimum.	9.0
	(vii) Calcium nitrate	traces
	(viii) <i>Particle size</i> The particle size of the material shall be such that 90 per cent of the material will be between -4 mm and +1 mm IS sieve.	
20. Nitrophosphate with Potash Grade II (15-15-15)	(i) Moisture per cent by weight maximum.	1.5
	(ii) Total nitrogen per cent by weight minimum.	15.0
	(iii) Neutral ammonium citrate soluble phosphate (as $P_2O_5$ ) per cent weight minimum.	15.0
	(iv) Water soluble phosphates (as $P_2O_5$ ) per cent by weight minimum.	4.0
	(v) Water soluble potash (as $K_2O$ ) per cent by weight minimum.	15.0
	(vi) <i>Particle size</i> The particle size of the material shall be such that 90 per cent of the material will be between -4mm and +1 mm IS sieve.	
21. Urea-ammonium Phosphate	(i) Moisture per cent by weight maximum.	1.0
	(ii) Total nitrogen per cent by weight minimum.	28.0

Name of the Fertilizer	Specifications	
	(iii) Ammoniacal nitrogen per cent by weight minimum	9.0
	(iv) Neutral ammonium citrate soluble phosphates (as $P_2O_5$ ) per cent by weight minimum	28.0
	(v) Water soluble phosphates (as $P_2O_5$ ) per cent by weight minimum.	25.0
	(vi) <i>Particle size</i> All the material shall pass through 3.35 mm IS sieve and 90 per cent will be retained on 1.18 mm IS sieve.	
22. Fused Calcium Magnesium Phosphate.	(i) Moisture per cent by weight maximum.	5.0
	(ii) Phosphate (as $P_2O_5$ ) soluble in two per cent citric acid solution, per cent by weight minimum.	15
	(iii) <i>Fineness</i>	
	(a) Retained on 150 micron IS sieve, per cent by weight	Nil
	(b) Passing 100 micron IS sieve, per cent by weight minimum.	80
23. Rock Phosphate.	(i) <i>Particle size</i> The material shall completely pass through 6.3 mm IS sieve and not less than 20 per cent of material shall pass through 150 micron IS sieve.	
	(ii) Total $P_2O_5$ content to be guaranteed by the dealer.	

#### B. Tolerance limit in plant nutrient for various fertilizers

1. For fertilizers with definite compounds like ammonium sulphate, urea, ammonium chloride, muriate of potash, sulphate of potash, superphosphate, dicalcium phosphate, which contain more than 20 per cent plant nutrients.	—0.2
For those which contain less than 20 per cent plant nutrients	—0.1
2. For calcium ammonium nitrate	—0.3
3. For diammonium phosphate, nitrophosphates, ammonium sulphate nitrate, urea ammonium phosphate, ammonium phosphate sulphate, bone meal, granulated mixed fertilizers, compound fertilisers.	—0.5 for individual nutrients subject to the maximum —2.5 per cent for all combined nutrients.

(9) After Schedule I to this Order, the following schedule shall be inserted namely:—

#### SCHEDULE II

(See clause 14A)

##### A. Procedure for Drawing Samples of Fertilisers

###### 1. General requirements of sampling

In drawing samples the following measures and precautions shall be observed :

- Samples shall not be taken at a place exposed to weather.
- The sampling instruments shall be clean and dry when used. (Diagram of the sample tube given separately).

- (c) The material being sampled, the sampling instruments and the containers for samples shall be protected from adventitious contaminations.
- (d) To draw a representative sample, the contents of each container selected for sampling shall be mixed as thoroughly as possible by suitable means.
- (e) The samples shall be placed in suitable, clean, dry and air-tight glass or other suitable containers.
- (f) The sample containers shall be of such a size that they are almost completely filled by the sample.
- (g) Each sample container shall be sealed air tight after filling, and marked with full details of sampling, the date of sampling and other important particulars of the consignment.
- (h) Samples shall be stored in shade.

## 2. Sampling from packages or containers.

### (a) Scale of sampling

- (i) *Lot*—All containers in a single consignment of the material of the same grade and type, drawn from a single batch of manufacture shall constitute a lot. If a consignment is declared to consist of different batches of manufacture, the batches shall be marked separately and the group of containers in each batch shall constitute separate lots. In the case of a consignment drawn from a continuous process, 1,000 containers (or 100 tonnes) of the material shall constitute a lot.
- (ii) The number of containers to be chosen from a lot shall depend on the size of the lot and shall be as given in Table below :—

*Number of Containers/Packages to be selected for Sampling*

Lot Size	Number of containers to be selected
N	n
(1)	(2)
2—8	2
9—27	3
28—64	4
65—100	5
101—300	6
301—500	7
501—800	8
801—1300	9
1301 and above	10



These containers shall be chosen at random from the lot, and in order to ensure randomness of selections a random number table as agreed to between the purchaser and the supplier shall be used. In case such a table is not available, the following procedure may be adopted:

Arrange all the containers in the lot in a systematic manner and starting from any container, count them as 1, 2, 3, ..... up to  $r$  and so on,  $r$  being equal to the integral part of  $N/n$ . Every  $r$ th container thus counted shall be with drawn and all such containers shall constitute the sample.

(b) *Preparation of composite samples*

- (i) Draw, with an appropriate sample instrument, small portions of the material from different parts of each container in the gross sample. The portions so obtained from the containers shall be mixed thoroughly and made into a composite sample.
- (ii) If the containers do not permit the use of sampling instrument, empty the contents of the containers on a level, clean, hard surface and draw a composite sample by the process of quartering as described under 2(b) (iii) below.
- (iii) If the composite sample is much larger than about 4 lb. (2 kg.) in weight, its size shall be reduced by the method of quartering. Spread the composite sample on a level, clean, hard surface, flatten it out and divide it into four equal parts. Remove any diagonally opposite parts.

Mix the two remaining parts together to form a cone, flatten out the cone and repeat the operation of quartering till a composite sample of about 4 lb. (2 kg.) in weight is obtained.

3. *Sampling from bulk in heaps or wagons*

(a) *Scale of sampling*

Samples shall be taken from each heap or wagon as the case may be.

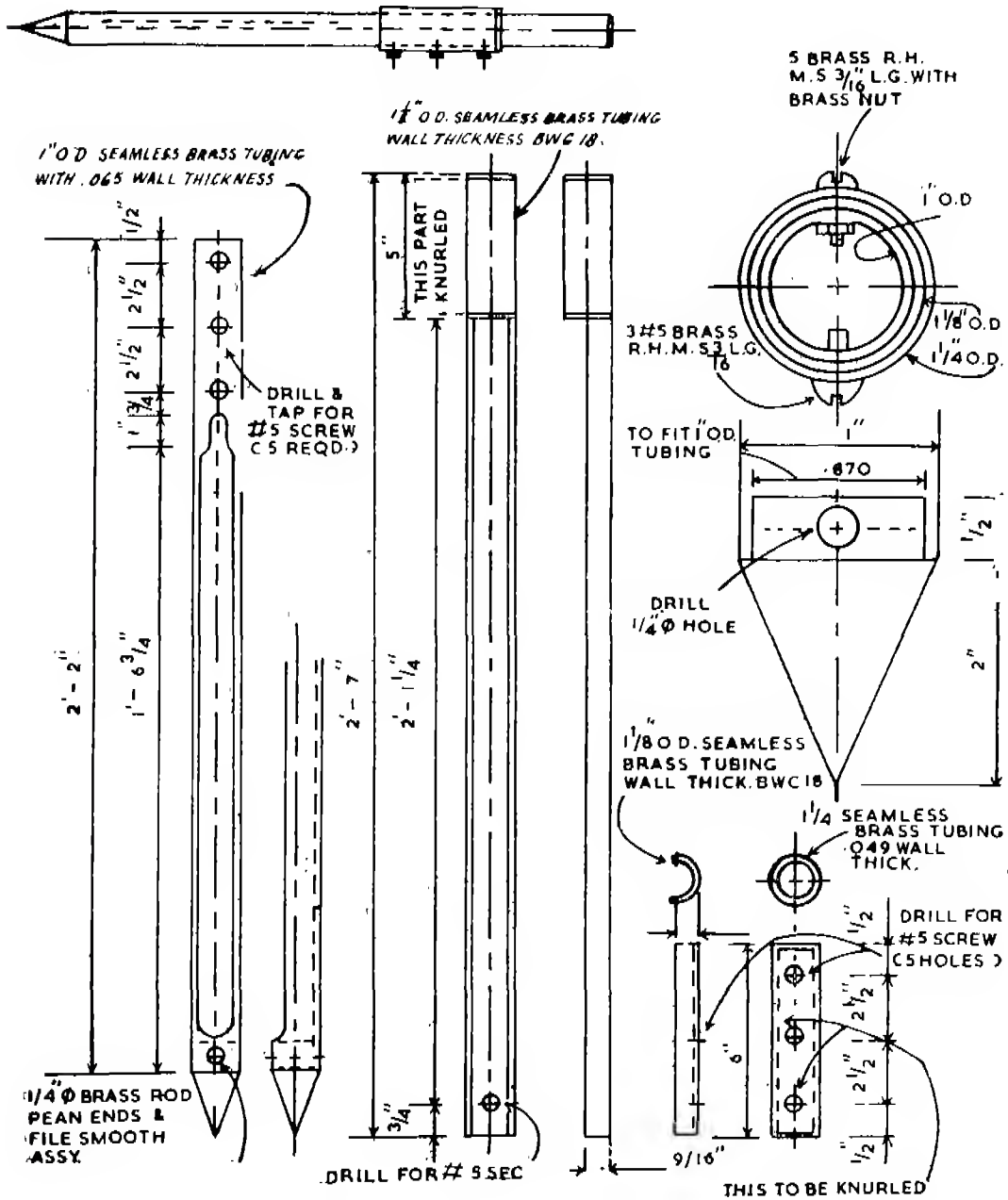
(b) *Preparation of composite samples*

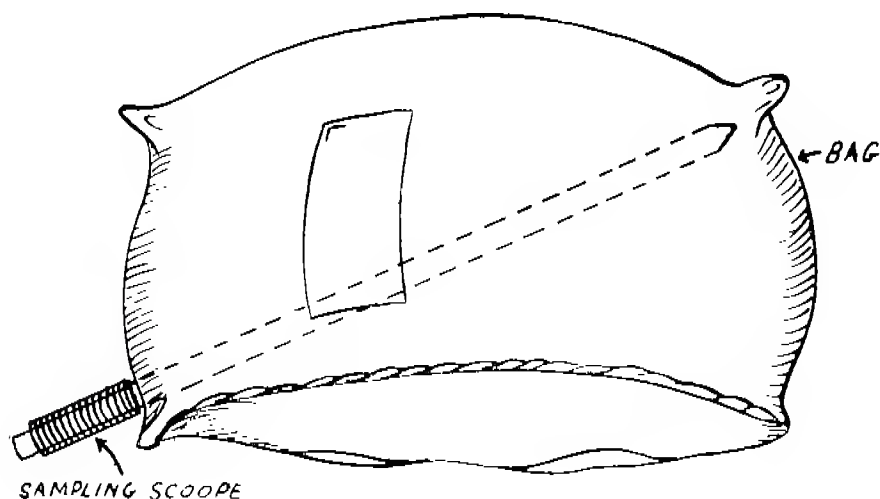
Draw several samples (at least 10) from each heap or wagon by means of a scoop from different parts, *viz.*, the front middle and back and at different depths so that the sample taken is representative of the bulk. Mix thoroughly the samples so collected on a clean, hard surface and draw a composite sample by the process of quartering as described under 2 (b) (iii) above.

4. *Test samples and reference sample*

(a) *Preparation of test samples*

- (i) The composite samples obtained under paras 2 or 3 above shall be spread out on a clean, hard surface and divided into three more or less equal portions not less than 1 lb. (0.5 kg.) each. Each of these samples shall constitute the test sample.
- (ii) Each test sample shall be immediately transferred to a suitable container, as described under 1(c) and 1(f), provided with a tight fitting stopper or lid so that the original composition of the fertiliser remains unchanged. Each container shall be properly labelled giving all the particulars of the consignment as described under 1 (g).
- (iii) Each test sample container shall then be sealed with seals of both the Inspecting Officer and the manufacturer or dealer or purchaser as the case may be.
- (iv) One sample so sealed shall be sent to the State Fertilizer Analyst or analysis and the second given to the manufacturer or dealer or purchaser as the case may be. The third sample shall constitute the reference sample and shall be retained by the Inspecting Officer for production in the Court, if necessary.





### B. Methods of Analysis of Fertilizers

#### 1. Preparation of sample for analysis in the laboratory

##### 1.1 Procedure

1. Reduce gross sample to quantity sufficient for analysis or grind not <0.5 lb. of reduced sample without previous sieving.
2. For fertiliser materials and moist fertiliser mixtures, that form a paste on putting pressure, grind in a porcelain pestle and mortar to pass sieve with 1 mm circular openings or No. 20 standard sieve.
3. For dry mixtures that tend to segregate, grind in a porcelain pestle and mortar to pass No. 40 standard sieve.
4. Grind as rapidly as possible to avoid loss or gain of moisture during operation.
5. Mix thoroughly and store in tightly stoppered bottles.

#### 2. Determination of moisture

(Not applicable to samples that yield volatile substances other than water at drying temperature).

##### 2.1 Procedure

1. Weigh to the nearest mg about 2 gm of the prepared sample in a weighed, clean, dry squat form weighing bottle.
2. Heat in an oven for about 5 hours at 99–101°C to constant weight. Cool in a desiccator and weigh.

#### Reagents

1. Iodine solution—Add 125 g n of iodine to a mixture of 650 ml. of methanol and 200 ml. of pyridine contained in a flask, and immediately close the flask tightly.
2. Sulphur dioxide solution—Pass dry sulphur dioxide into 100 ml. of pyridine contained in a 250 ml. graduated cylinder and cooled in an ice bath, until the volume reaches 200 ml.
3. Fischer Reagent—Slowly add iodine solution to the cooled sulphur dioxide solution stopper immediately and shake well until the iodine is dissolved. Transfer the solution to an automatic pipette, protected from absorption of moisture by a drying agent and allow to stand for 24 hours before standardising. The reagent deteriorates continuously and it should be standardized within one hour before use.

3. In case of sodium nitrate, ammonium sulphate and potassium salts heat to constant weight at 129—131°C.

4. Report percentage loss in weight as moisture at temperature used.

#### Calculations

Free moisture percent

$$\text{by weight} = \frac{100 \times B - C}{B - A}$$

A = Weight of the bottle.

B = Weight of the bottle plus material before drying.

C = Weight of the bottle plus material after drying.

(Reference "Methods of Analysis", AOAC, 1965)

#### 2.2 Moisture in Ammonium Chloride

1. Weigh accurately about 5 gm. of prepared sample in a weighed shallow porcelain dish and dry for 24 hours in a vacuum desiccator over sulphuric acid and re-weigh.

2. Preserve the dried material for subsequent tests.

#### Calculations

$$\text{Moisture percent by weight} = 100 \times \frac{W_1}{W_3}$$

$W_1$  = loss in weight in gm. on drying, and

$W_3$  = weight in gm. of the prepared sample taken for the test.

2.3 Samples like urea, diammonium phosphate and ammonium nitrate which yield volatile substances other than water at drying temperature, the Karl Fischer method given below is used for the determination of moisture.

4. Standard water solution—Measure exactly 2 ml. of water into a thoroughly dry 1 litre volumetric flask, dilute to volume with methanol. Retain sufficient quantity of the same methanol for a blank determination. Keep the solution in tightly closed containers.

#### Procedure

1. Determination of End point in Karl Fischer Titration—In many cases, the end point can be detected visually by the change of colour from a light brownish yellow to amber. But when the end point is not clearly defined, the electrometric method for determining the end point should be adopted. Adjust the potentiometer so that when a small excess (0.02 ml.) of the reagent is present, a current of 50 to 150 microampers is recorded. The solution should be continuously and vigorously stirred. At the beginning of the titration, a current of only a few microampers will flow. After each addition of reagent, the pointer of the micrometer is deflected but rapidly returns to the original position. At the end point a deflection is obtained which endures for a longer period.

2. Standardization of the Fischer reagent—Pipette exactly 10 ml. of methanol into a dry titration flask and titrate with the Fischer reagent to the end point. The pipette exactly 10 ml of the standard water solution into the flask and titrate to the end point.

3. Titration of the material—Transfer 25 ml. of methanol to the titration flask and titrate to the end point with the Fischer reagent. Do not record the volume consumed. Quickly transfer to the titrated liquid an accurately weighed quantity of the material containing 10 to 50 mg. of water, stir vigorously and titrate to the end point.

*Calculation*

$$\text{Moisture percent by weight} = \frac{0.1 \times W (V_2 - 2.5V_1)}{(V_2 - V_1)A}$$

where

$W$  = weight in mg of water contained in 10 ml. of standard water solution

$V_2$  = total volume in ml. of the reagent used in titration in (3).

$V_1$  = volume in ml of reagent used in titration of methanol in (2) and

$V_2$  = total volume in ml. of the reagent used in titration in (ii)

$A$  = weight in gm of the material taken for the test in (3)

(Reference I.S. Specification for urea, technical and pure, I.S. 1781—1961)

### 3. *Determination of nitrogen.*

Methods of determination of total nitrogen, ammoniacal nitrogen, nitrate nitrogen, and urea nitrogen have been described separately in this section. These methods can be adopted both for straight and mixed fertilisers. Scope of each method with various combinations have also been described with each method.

The relevant methods of analysis which have been described are as given below :

1. Total Nitrogen—for nitrate free samples.
2. Total Nitrogen—for nitrate containing samples.
3. Total nitrogen—for materials with high  $\text{Cl}:\text{NO}_3$  ratio and to materials containing only water-soluble nitrogen.
4. Determination of ammoniacal nitrogen.
5. Determination of ammoniacal and nitrate nitrogen.
6. Determination of nitrate nitrogen.
7. Determination of water insoluble nitrogen.
8. Determination of urea nitrogen.

#### 3.1 *Detection of nitrate*

For adopting a specific method as described above, it is necessary to detect the presence of nitrates in the sample before a particular method is adopted. The procedure for detection of nitrates is given below.

1. Mix 5 gm sample with 25 ml. hot water and filter.
2. To one volume of this solution add 2 volume of sulphuric acid, free from  $\text{HNO}_3$  and oxides of N, and let it cool.
3. Add a few drops of concentrated  $\text{FeSO}_4$  solution in such a manner that fluids do not mix.
4. If the nitrates are present junction shows at first purple, afterward brown, or if only minute quantity is present, reddish colour.
5. To another portion of solution add 1 ml. 1 per cent  $\text{Na}_2\text{NO}_3$  and test as before to determine whether enough  $\text{H}_2\text{SO}_4$  was added in the first test.

(Reference "Methods of Analysis" AOAC., 1965)

#### 3.2 *Reagents for determination of total nitrogen*

- (i) Sulphuric acid—93-98 percent  $\text{H}_2\text{SO}_4$ , N free.
- (ii) Copper sulphate —  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  reagent grade, N free.
- (iii) Potassium sulphate (or anhydrous sodium sulphate)—reagent grade.
- (iv) Salicylic acid—reagent grade, N free.
- (v) Sulphide or thiosulphate solution—Dissolve 40 gm. commercial  $\text{K}_2\text{S}$  in 1 litre distilled water.

(Solution—of 40 gm.  $\text{Na}_2\text{S}$  or 80 gm  $\text{Na}_2\text{S}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$  in 1 litre may be used).

- (vi) Sodium hydroxide—Pellets or solution, nitrate free. For solution dissolve approximately 450 gm solid NaOH in distilled water and dilute to 1 litre (Sp. gr. of solution should be 1.36 or higher).
- (vii) Zinc granule—reagent grade.
- (viii) Zinc dust—Impalpable powder.
- (ix) Methyl red indicator—Dissolve 1 gm. methyl red in 200 ml. alcohol.
- (x) Hydrochloric or sulphuric acid standard solution, 0.5N or 0.1N when amount of N is small.
- (xi) Sodium hydroxide standard solution—0.1 N (or other specified concentration).

1. Standardize each standard solution with primary standard and check one against another.

2. Test reagents before using, by blank determination with 2 gm. sugar which insures partial reduction of any nitrates present.

Caution : Use freshly opened sulphuric acid or add dry  $\text{P}_2\text{O}_5$  to avoid hydrolysis of nitriles and Cyanates. Ratio of salt to acid (wt. Vol) should be approximately 1 : 1 at end of digestion for proper temperature control. Digestion may be incomplete at lower ratio, N may be lost at higher ratio.

### 3.3 Apparatus

- (a) For digestion—Use Kjeldahl flask of hard moderately thick, well annealed glass with total capacity approximately 500-800 ml. Conduct digestion over heating device, adjusted to bring 250 ml. water at  $25^\circ\text{C}$  to rolling boil in approximately for 5 minutes. Add 3-4 boiling chips to prevent superheating.
- (b) For distillation—Use Kjeldahl or other suitable flask of 500-800 ml. capacity filled with rubber stopper through which passes lower end of efficient scrubber bulb or trap to prevent mechanical carryover of NaOH during distillation. Connect upper end of bulb tube to condenser tube by rubber tubing. Trap outlet of condenser in such a way as to insure complete absorption of ammonia distilled over into acid in receiver.

### 3.4 Total nitrogen (in nitrate free samples)

#### Procedure

- 1. Place weighed sample (0.7-2.2 gm.) in digestion flask.
- 2. Add 0.7 gm. copper sulphate, 15 gm. powdered  $\text{K}_2\text{SO}_4$  or anhydrous  $\text{Na}_2\text{SO}_4$ , and 25 ml.  $\text{H}_2\text{SO}_4$ .
- 3. If sample more than 2.2 gm. is used, increase sulphuric acid by 10 ml. for each gm. sample.
- 4. Place flask in inclined position and heat gently until frothing ceases (if necessary add small amount of paraffin to reduce frothing).
- 5. Boil briskly until solution clears and then for at least 30 minutes longer (2 hours for sample containing organic material).
- 6. Cool add approximately 200 ml. distilled water, [cool below  $25^\circ\text{C}$ ].

7. Add to the flask a layer of sodium hydroxide (25 gm solid reagent or enough solution to make contents strongly alkaline) without agitation.
8. Immediately connect flask to distilling bulb or condenser and with tip of condense immerse in standard acid in receiver.
9. Rotate flask to mix contents thoroughly, then heat until all ammonia has distilled (at least 150 ml distillate).
10. Titrate excess standard acid in distillate with standard sodium hydroxide solution, using methyl red as an indicator.
11. Correct for blank determination on reagents.

#### Calculation

$$\text{Percent Nitrogen} = \frac{(A N_a - B N_b) \times 0.01401 \times 100}{W}$$

A = ml. of standard acid used.

B = ml. of standard NaOH used.

N<sub>a</sub> = Normality of standard acid.

N<sub>b</sub> = Normality of standard NaOH.

W = Weight of the sample taken in grams.

(Reference "Methods of Analysis", A.O.A.C., 1965).

#### 3.5. Total Nitrogen (for nitrate containing samples)

(Not applicable to samples containing high concentrations of nitrate nitrogen and chlorides)

#### Procedure

1. Place weighed sample (0.7—2.2 gm) in digestion flask.
2. Add 40 ml. H<sub>2</sub>SO<sub>4</sub> containing 2 grams salicylic acid. Shake until thoroughly mixed and let stand, with occasional shaking, 30 minutes or more.
3. Then add (i) 5 grams Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> · 5H<sub>2</sub>O or (ii) 2 grams zinc dust (as unpalpable powder not granulated zinc or filings).
4. Shake the flask and let it stand for five minutes, then heat over low flame until forthing ceases.
5. Turn off heat, add 0.7 grms copper sulphate, 15 gm. powdered K<sub>2</sub>SO<sub>4</sub> (or anhydrous Na<sub>2</sub>SO<sub>4</sub>), and boil briskly until solution clears, then at least 30 minutes longer (2 hours for samples containing organic material).

Proceed further as in 6-11 of 3.4.

#### Calculations

Same as in 3.4.

(Reference "Methods of Analysis"—A.O.A.C., 1965).

#### 3.6. Total nitrogen (for materials with high Cl: NO<sub>3</sub> ratio and to materials containing only water soluble nitrogen).

#### Reagents

Reduced iron powder, electrically reduced, N.F. (National Formulary). For other reagents see 3.2.

#### Procedure

#### Mixed Fertilisers

1. Place 0.5—2.0 gm sample in Kjeldahl flask and add 2-5 grams. reduced Fe (5 grms. is enough for 0.185 grms. NO<sub>3</sub>).

2. Add approximately 25 ml. distilled water, rotating flask at angle to wash down the sample.
3. Let it stand for 15 minutes with occasional agitation, to insure complete solution of all soluble salts.
4. While rotating flask add 25 ml. cold  $H_2SO_4$  (1+1) and let it stand until visible reaction ceases. (Use hood or vented digestion unit).
5. Add boiling chips and boil 15—20 minutes, but do not take to dryness. (For samples containing organic matter, use 50 ml. cold  $H_2SO_4$  (1+1), boil for 15—20 minutes, add 0.7 gm.  $HgO$  and heat again for 30 minutes). Cool and proceed further as in 6—11 of 3.4.

#### Calculations

Same as in 3.4

(Reference "Methods of Analysis", A.O.A.C., 1965).

### 3.7. Determination of ammoniacal nitrogen (Distillation Method.)

(This method is for the determination of nitrogen present or available in the sample as ammonium ion. This method assumes that Urea is absent from the sample. Not applicable to  $MgNH_4PO_4$  and  $FeNH_4PO_4$ .)

#### Procedure

1. Place 0.7—3.5. grms; according to  $NH_3$  content of the sample, in distillation flask with approximately 300 ml. water and 2 grms. of freshly ignited carbonate free  $MgO$  or  $NaOH$  solution.
2. Connect the flask to condenser by Kjeldahl connecting bulb.
3. Distill 100 ml. liquid into measured quantity of standard acid and titrate with standard  $NaOH$  solution, using methyl red as an indicator.

#### Calculations

$$\text{Percent Nitrogen} = \frac{(ANa - BNb) \times 0.01401 \times 100}{W}$$

A—ml. of standard acid used.

B—ml. of standard  $NaOH$ .

Na—normality of acid.

Nb—normality of  $NaOH$

W—weight of the sample taken in grms.

(Reference (Recommended analytical methods of the National Plant Food Institute, Washington, D. C., 1951).

### 3.8. Determination of ammoniacal and nitrate nitrogen

#### Devarda Method

(This method is for the determination of total nitrogen when only nitrate or mixture of nitrate and ammoniacal nitrogen is present. This method assumes the absence of Urea, Calcium Cyanamide Cyanamide and organic matter from the sample).

#### Procedure

1. Place 0.35—0.5 grms. sample in 600—700 ml. flask and add 300 ml. water, 3 grms. Devarda alloy, and 5 ml.  $NaOH$  solution (42 percent by weight pouring later down side of flask so that it does not mix at once with contents).
2. Allow the flask to stand for 15 minutes.
3. By means of Davison (J Ind Eng. Chem. 11, 465. (1919)) or other suitable scrubbing bulb that will prevent passing over of any spray connect with condenser, tip of which always extends beneath surface of standard acid in receiving flask.
4. Mix contents of distilling flask by rotating.
5. Heat slowly at first, and then at a rate to yield 250 ml. distillate in 1 hour.



6. Collect distillate in measured quantity of standard acid and titrate with standard NaOH solution, using methyl red as an indicator.

7. In analysis of nitrate salts dissolve 3.5 or 5.0 grms. in water, to 250 ml and use 25 ml aliquot.

#### Calculations

Same as in 3.4

(Reference "Methods of Analysis", AOAC)

#### 3.9 Determination of nitrate nitrogen

(Applicable in presence of calcium cyanamide and urea in the mixture).

#### Procedure

(a) Determine total nitrogen as in 3.5.

(b) Determine water insoluble N as in 3.10 but use 2.5 grms. sample. Dilute to 250 ml.

(c) Determine amoniacal N in 50 ml filtrate as in 8.7

(d) Place another 50 ml portion filtrate in 500 ml Kjeldah flask and 2 grms.  $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$  and 20 ml  $\text{H}_2\text{SO}_4$ . (If total N is 5 percent use 5 gm  $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$ ). Digest over hot flame until all water is evaporated and white fumes appear and continue digestion at least ten minutes to drive off Nitrate N. If severe bumping occurs, add 10-15 glass beads. Add 0.65 grms. Hg or 0.7 grms  $\text{HgO}$  and digest until all organic matter is oxidized cool, dilute add the  $\text{K}_2\text{S}$  solution and complete determination as 3.4. Before distillation add pinch of mixture of Zinc dust and granular "20 mesh", Zinc to each flask to prevent bumping.

#### Calculations

Total N (a)—water insoluble N (b)=water soluble N.

Water sol N—N obtained in (d)=Nitrate N.

(Reference Methods of Analysis A.O.A.C., 1965).

#### 3.10 Determination of water insoluble nitrogen

#### Procedure

1. Place 1 or 1.4 grms. sample in 50 ml. breaker, wet with alcohol.

2. Add 20 ml. water and let it stand for 15 minutes, stirring occasionally.

3. Transfer supernatant liquid to 11 cm. Watman No. 42 paper in  $60^\circ$  long stem funnel 2.5" diameter and wash residue 4 or 5 times by decanting with water at room temperature (20-25° C).

4. Finally transfer all residue to filter and [complete] washing until filtrate measures 250 ml.

5. Determine N as in 3.4.

#### 3.11 Determination of Urea nitrogen

(This method is for the determination of urea content of any mixed fertilizer)

#### Reagents

1. Neutral urcase solution—shake 1 gm jack bean meal with 100 ml. water for 5 minutes. Transfer 10 ml. solution to 250 ml. erlenmeyer flask, dilute with 50 ml. water and add 4 drops methyl purple indicator. Titrate with 0.1 N HCl to reddish purple, then back titrate to green with 0.1 N NaOH. From difference in ml., calculate amount of 0.1 N HCl required to neutralize remainder of solution (usually approximately 2.5 ml. per 100 ml) add this amount of acid and shake well.

*Procedure*

1. Weight  $10 \pm 0.01$  gm. sample and transfer to 15 cm. whatman No. 12 fluted filter paper.
2. Leach with approximately 300 ml. water into 500 ml volumetric flask.
3. Add 75-100 ml. saturated barium hydroxide solution to precipitate phosphates.
4. Let it settle and test for complete precipitation with few drops of saturated barium hydroxide solution.
5. Add 20 ml. 10 per cent sodium carbonate solution to precipitate excess barium and any soluble calcium salts.
6. Let it settle and test for complete precipitation.
7. Dilute to volume, mix and filter through 15 cm. whatman No. 12 fluted paper.
8. Transfer 50 ml aliquot (equivalent to 1 gm. sample) to 200 or 250 ml. erlenmeyer flask and add 1 to 2 drops methyl 1 purple indicator.
9. Acidify solution with 2NHCl and add 2 to 3 drops excess.
10. Neutralize solution with 1 O. 1 N NaOH to first change in colour indicator.
11. Add 20 ml neutral urease solution, close flask with rubber stopper and let it stand for 2 hour at  $20-25^{\circ}\text{C}$ .
12. Cool the flask in ice water slurry and titrate at once with 0.1 Ncl to full purple colour, then add approximately 5 ml, excess.
13. Record total volume added, back titrate excess HCl with 0.1 N NaOH to neutral end point.

*Calculations*

Percentage urea =  $(\text{ml } 0.1 \text{ N HCl} - \text{ml } 0.1 \text{ N NaOH}) \times 0.3003 / \text{wt. of the sample}$ .

(Reference "Methods of Analysis" A. O. A. C., 1965).

*3.12 Determination of biuret**Reagents*

1. Alkaline tartarate solution—Dissolve 40 gm. Na OH in 50 ml. water cool, add 50 gm of  $\text{Na}_2\text{K}_2\text{C}_4\text{H}_6\text{O}_6 \cdot 4 \text{H}_2\text{O}$  and dilute to 1 litre. Let it stand for one day before use.
2. Copper sulphate solution—Dissolve 15 gm  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in  $\text{CO}_2$  free water and dilute to 1 litre.
3. Biuret standard solution—1 mg/ml. Dissolve 100 mg reagent grade biuret in  $\text{CO}_2$  free water and, dilute to 100 ml.
4. Ion exchange resin. Fill 50 ml. burette with 30 cm column of Amberlite IR 120 (H) resin on glass wool plug. Regenerate column after each use by passing 100 ml  $\text{H}_2\text{SO}_4$  (1+9) or 12(1+4) through the column approximately 5 ml. per minute and then washing with water until pH of effluent is 7.6.

*Preparation of standard curve*

1. Transfer series of aliquots, 2-50 ml. of standard biuret solution to 100 ml. volumetric flask.
2. Adjust volume to approximately 50 ml with  $\text{CO}_2$  free water. Add one drop of methyl red and neutralize with 0.1 N  $\text{H}_2\text{SO}_4$  to pink colour.
3. Add with swirling 20 ml. alkaline tartarate solution and then 20 ml  $\text{CuSO}_4$  solution.
4. Dilute to volume. Shake for 10 seconds and place in water bath for 15 minutes at  $30 \pm .50^{\circ}\text{C}$ .

5. Also prepare reagent blank.

6. Determine absorbance of each solution against blank at 555 mμ (instrument with 500-570mμ filter is also satisfactory) with 2-4 cm. cell, and plot standard curve.

#### Procedure

##### *In urea*

1. Stir continuously 2-5 gm sample in 100 ml approximately 50° C water for 30 minutes.
2. Filter and wash into 250 ml volumetric flask and dilute to volume.
3. Transfer 25 ml aliquot to 100 ml volumetric flask and proceed as given under preparation of standard curve 3.12.

##### *In mixed fertilisers*

1. Stir continuously 10-20 gm sample in 150 ml approximately (50° C) hot water for 30 minutes.
2. Filter and wash into 250 ml volumetric flask and dilute to volume.
3. transfer 25 ml aliquot to column 3.12 (4) and adjust flow to 4-5 ml/minute.
4. Receive eluate in 100 ml beaker.
5. When liquid level falls to top of resin bed, wash with two 25 ml portion water.
6. To eluate and washings add two drops of methyl red and then IN NaOH to yellow colour.
7. Add 0.1 N<sub>2</sub>SO<sub>4</sub> until solution just turns pink.
8. Transfer to 100 ml. volumetric flask and dilute to volume with CO<sub>2</sub> free water.
9. Transfer 50 ml aliquot to 100 ml volumetric flask and proceed as in preparation of standard curve given above.

#### Calculations

From standard curve determine concentration of biuret in final dilution, then per cent of

$$\text{biuret} = \frac{C \times 100}{W}$$

where C = Concentration in mg/ml of biuret in final dilution obtained from standard curve

W = Concentration of original sample in final dilution expressed as mg/ml.

(Reference "Methods of Analysis" A. O. A. C.)

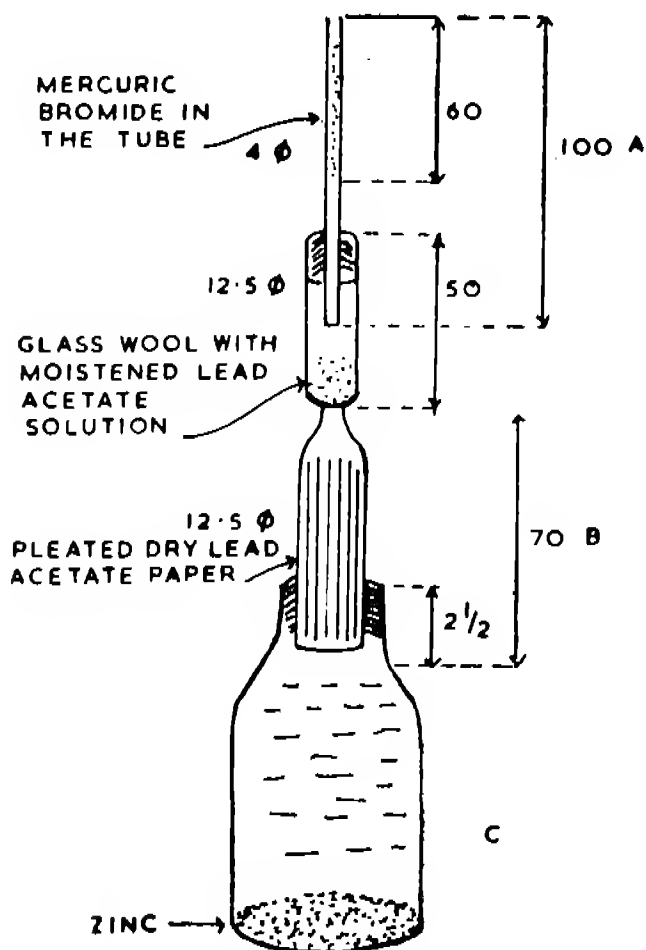
#### 3.13 Determination of free acidity in ammonium sulphate (as H<sub>2</sub>SO<sub>4</sub>)

##### *Reagents*

1. Standard sodium hydroxide solution—0.02 N
2. Methyl red indicator—Dissolve 0.15 gm of water soluble methyl red in 500 ml water.
3. Methyl red—Methyl blue mixed indicator solution—prepared by mixing equal volumes of 0.2 per cent solution in rectified spirit of methyl red and 0.1 per cent solution in rectified spirit of methylene blue.

##### *Procedure*

1. Dissolve about 20 gm of prepared sample, accurately weighed in about 50 ml cold natural water.
2. Filter and make up the volume to about 200 ml.
3. Titrate with standard sodium hydroxide solution, using one or two drops of methyl red as indicator.
4. If satisfactory end point with methyl red is not obtained, methylene red—methylene blue mixed indicator may be used.



5. Use preferably a micro biuret for this titration.

\*The filtering medium shall be neutral and shall not contain any alkaline material which would neutralize free acid.

#### Calculations

$$\text{Free acidity as H}_2\text{SO}_4 \text{ per cent by weight} = \frac{4.904 \text{ AN}}{V}$$

A=Volume of ml of standard NaOH solution.

N=Normality of standard Na OH solution.

W=Weight in gm of prepared sample taken for the test.

(Reference—Specifications for ammonium sulphate, fertilizer grade IS:826-1967)

#### 3.14 Determination of Arsenic in Ammonium sulphate (as $\text{As}_2\text{O}_3$ ).

##### Reagents

1. Lead acetate solution—Prepare 10 per cent solution of lead acetate with sufficient acetic acid added to clear the solution.

2. Dry lead acetate paper—Cut filter paper (Whatman No. 1 or equivalent) into strips  $70 \times 50$  mm and keep them permanently suspended in lead acetate solution in a glass stoppered bottle. Before use, take out the strips and dry them in an atmosphere free from hydrogen sulphide.

3. Mercuric Bromide solution—Dissolve 5 gm of mercuric bromide in 100 ml rectified spirit.

4. Sensitized Mercuric Bromide paper strips—cut filter paper (Whatman No. 1 or equivalent) into strips  $120 \times 2.5$  mm. Keep the strips permanently suspended in dark in a glass stoppered cylinder or amber bottle having mercuric bromide solution. Before use take out a strip, press it between sheets of filter paper and dry it in an atmosphere free from hydrogen sulphide.

5. Dilute sulphuric acid—approximately 5 N.

6. Concentrated hydrochloric acid.

7. Potassium iodide solution—15 per cent.

8. Stannous chloride solution—Dissolve 80 gm of stannous chloride in 100 ml. water containing 5 ml. of concentrated hydrochloric acid. If the solution is turbid add a few ml. of more hydrochloric acid and boil until clear solution is obtained. Add some metallic tin to the solution to prevent oxidation.

9. Zinc—It is recommended that zinc rods prepared as described below should be used. For routine work, however, pellets described may be used.

##### Preparation of zinc rods

1. Take a clean and dry hard glass test tube of 10 mm internal diameter and 20 cm. length.  
2. Heat the test tube over a flame of Bunsen or blow pipe burner and add slowly arsenic free granulated zinc in small portions (1 to 2 gm at a time) the next portion being added after the first one has completely melted.

3. Continue heating and adding zinc until the melt is about 10 cm high.

4. Heat the clean melt for half an hour and then cool to room temperature.

5. Break the tube to obtain the rod of zinc.

6. Cut rod into pieces 20 mm long.

7. Coat the plane ends of the pieces with a paste of magnesium carbonates and gum arabic solution and dry.

8. Coat the pieces all over with 1.5 mm thick layer of paraffin wax.

9. When required for use, scrap off the wax from the plane ends with a knife, protecting wax colour round the rods.

10. Remove the paste from the plane ends by soaking in water and activate the exposed surface by dipping in a solution containing one part of stannous chloride solution and seven parts of concentrated hydrochloric acid.

#### *Preparation of zinc pellets*

Treat zinc shots passing through IS sieve 570 (aperture 5660 microns) and retained on IS sieve 280 (aperture 2818 microns) with concentrated hydrochloric acid until the surface of zinc becomes clean and dull. Weigh and keep under water, preventing contamination with dust.

10. Standard sodium hydroxide solution—approximately 20 per cent.

#### *11. Standard arsenic trioxide solution*

1. Dissolve 1.0 gm of resublimed arsenic trioxide ( $As_2O_3$ ) in 25 ml sodium hydroxide solution and neutralize with dilute sulphuric acid.

2. Dilute with freshly distilled water containing 10 ml of concentrated sulphuric acid per litre and make up the volume to 1 litre.

3. Again dilute 10 ml of this solution to 1 litre with water containing sulphuric acid and finally dilute 100 ml of this solution to 1 litre with water containing sulphuric acid. One ml of this solution contains 0.001 mg of arsenic trioxide ( $As_2O_3$ ). The dilute solution shall be prepared freshly when required.

#### *Procedure*

1. Dissolve 1.0 gm of the prepared sample in 20 ml water.

2. Place dry lead acetate paper in the lower portion of the tube B (in fig.) and glass wool moistened with lead acetate solution in its proper portion.

3. Place the sensitized strips of mercuric bromide paper in tube A and connect the tubes together with a rubber stopper.

4. Introduce the solution of the material into the bottle C (120 ml) and then add 10 ml of dilute sulphuric acid. Add 0.5 ml of stannous chloride solution 5 ml potassium iodide solution and make up the volume with water to about 50 ml.

5. Mix the contents and drop about 10 gm of zinc. Immediately fit in position the rubber stopper carrying the tube B.

6. Place the bottle in a warm place at about 40°C.

7. At the end of two hours remove the test strip by means of tweezers.

8. Carry out the test prescribed above using a volume of standard arsenic trioxide solution containing 0.1 mg of arsenic trioxide, in place of the solution of the material and compare the stain produced with the material with that produced with arsenic trioxide solution.

9. The limit prescribed in the material specification shall be taken as not having been exceeded if the length of the stain as well as the intensity of its colour produced in the test with the material is not greater than those produced with the arsenic solution.

(Reference "Modified Gutzet method of test for arsenic" IS-2088—1962).

#### *3.15 Determination of calcium nitrate (for calcium ammonium nitrate and nitrophosphates).*

#### *Reagents*

1. n-Amyl Alcohol—

2. Dilute hydrochloric acid—approximately 4N.

3. Standard calcium solution—weigh 1.0 gm of calcium carbonate dried at  $120 \pm 5^\circ\text{C}$  and dissolve in the minimum quantity of dilute hydrochloric acid. Dilute the solution to 1 litre in a graduated flask.

4. Ammonium chloride—ammonium hydroxide buffer solution. Dissolve 67.5 gm ammonium chloride in a mixture of 570 ml of ammonium hydroxide (sp. gr. 0.92) and 250 ml water. Also dissolve separately a mixture of 0.931 gm of disodium ethylene diamine tetra-acetate dihydrate and 0.616 gm of magnesium sulphate ( $MgSO_4 \cdot 7H_2O$ ) in about 50 ml of water. Mix the two solutions and dilute to 1 litre.

5. Standard Disodium ethylene diamine Tetra-acetate (EDTA) solution—weigh 3.72 gm of disodium ethylene diamine tetra-acetate dihydrate in water, and dilute in a graduated flask to 1 litre. The solution shall be standardized frequently against standard calcium solution following the procedure given below.

6. Eriochrome Black T Indicator solution—Dissolve 0.1 gm in 20 ml of rectified spirit. The solution shall be used for not more than a week.

*Procedure*

1. Grind quickly about 5 gm of the material, accurately weighed, with about 50 ml of amyl alcohol in a pestle and mortar and transfer the contents to a conical flask.
2. Wash the pestle and mortar with a few ml of amyl alcohol and add the washings to the flask.
3. Shake the contents of the flask manually or in a mechanical shaker for about half an hour and then filter.
4. Transfer the filtrate to a separating funnel and extract calcium nitrate completely with water in five to six instalments.
5. A few drops of dilute hydrochloric acid may be added during the extraction with water to avoid formation of an emulsion of amyl alcohol with water.
6. Concentrate the water extract at low temperature to nearly half its volume.
7. Transfer the concentrated solution to a conical flask, and 5 ml of ammonium chloride—ammonium hydroxide buffer solution, 5 drops of eriochrome black T indicator solution and titrate against standard EDTA solution to a pure blue end point.

*Calculations*

$$\text{Calcium nitrate per cent by weight} = \frac{8.2 \text{ NV}}{W}$$

Where N=normality of standard EDTA solution

V=Volume in ml of standard EDTA solution used in the titration, and

W=Weight in gm of the material taken for test.

(Reference : IS specifications of CAN IS : 2409-1963)

*3.16 Determination of Chlorides other than ammonium chloride.*  
*Reagents*

1. Standard silver nitrate solution—0.1 N
2. Concentrated nitric acid—conforming to IS: 264-1950
3. Ferrous ammonium sulphate solution saturated in water and stabilized by addition of 50 ml nitric acid.
4. Standard Ammonium thiocyanate/solution—0.1 N

*Procedure*

1. Dissolve about 0.2 gm of the prepared sample, previously dried as in procedure for determination of moisture and accurately weighed, in about 40 ml water.
2. Add exactly 50 ml of standard silver nitrate solution and 5 ml of concentrated nitric acid.
3. Add 0.5 ml of nitrobenzene and make up the volume of the mixture to exactly 100 ml with water.
4. Take exactly 50 ml of the solution and add 2 ml of ferric ammonium sulphate solution.
5. Titrate the excess of silver nitrate in this portion with standard ammonium thiocyanate solution.
6. Carry out a blank test following the procedure given as above but without using the material.

*Calculations*

Total chlorides (as cl) per cent

$$\text{by weight (on dry basic)} = \frac{7.07 (V_1 - V_2) N}{W} \times$$

where

V<sub>1</sub>=Volume in ml of standard ammonium thiocyanate used in the blank determination.

V<sub>2</sub>=Volume in ml of standard ammonium thiocyanate solution used in the test with the material.

N= Normality of standard ammonium thiocyanate solution.

W=Weight in gm of the dried prepared sample taken for the test.

Express the ammoniacal nitrogen content per cent by weight of the material determined earlier in terms of Cl as follows :

Chloride equivalent of the ammoniacal nitrogen content,

per cent by weight =  $2.531 \times A \dots\dots Y$

where  $A$  is the ammoniacal nitrogen content determined earlier.

Balanced chloride equivalent to sodium chloride ( $\text{NaCl}$ ) percent by weight =  $1.648 \times (x-y)$ .

$(x-y)$  = Balanced chlorides other than ammonium chloride.

(Reference IS Specification for ammonium chloride fertiliser grade (Revised) IS: 1114-1964 calculations modified.)

#### 4. Determination of phosphates

Methods of determination of total phosphates, water soluble phosphates, citrate soluble phosphates, citrate insoluble phosphates and citric acid soluble phosphates have been described separately in this section. These methods are applicable to straight as well as mixed phosphatic fertilisers.

##### 4.1 Preparation of solution of the samples

(Separate methods of preparing solutions of the samples have been described according to the nature of the sample).

##### Reagent

Magnesium nitrate solution—Dissolve 950 gm

P—free  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in water and dilute to 1 litre.

##### Procedure

1. Treat 1 gms sample by (a), (b), (c), (d) or (e) method depending on the nature of the sample.
2. Cool solution transfer to 200 to 250 ml volumetric flask, dilute to volume, mix and filter through dry filter.
  - (a) (Suitable for materials containing small quantities of organic matter). Dissolve in 30 ml  $\text{HNO}_3$  and 3—5 ml  $\text{HCl}$  and boil until organic matter is destroyed.
  - (b) (Suitable for fertilisers containing much Fe or Al phosphate and basic slag). Dissolve in 15—30 ml  $\text{HCl}$  and 3—10 ml  $\text{HNO}_3$ .
  - (c) (Suitable for organic material like cotton seed meal alone or in mixture). Evaporate with 5 ml of the  $\text{Mg}(\text{NO}_3)_2$  solution, ignite and dissolve in  $\text{HCl}$ .
  - (d) (Generally applicable to materials or mixtures containing large quantities of organic matter). Boil with 20—30 ml  $\text{H}_2\text{SO}_4$  in 200 ml flask adding 2—4 gm of  $\text{NaNO}_3$ ,  $\text{KNO}_3$  at beginning of digestion and small quantity after solution is nearly colourless, or adding the nitrate in small portions from time to time. When solution is colourless, cool add 150 ml water and boil for few minutes. Before adding  $\text{NaNO}_3$  or  $\text{KNO}_3$ , let mixture digest, at gentle heat if necessary, until violence of reaction is over.
  - (e) (Suitable for all fertilisers). Boil gently for 30—45 minutes with 20—30 ml  $\text{HNO}_3$  in a suitable flask (Preferably a Kjeldahl for samples containing large quantities of organic matter to oxidize all easily oxidizable matter). Cool and add 10—20 ml of 70—72 per cent perchloric acid. Boil very gently until solution is colourless or nearly so and white dense fumes appear in flask. Do not boil to dryness at any time (Danger I). (With samples containing large quantities of organic matter temperature should be raised to fuming point approximately  $170^\circ\text{C}$ , over a period of 1 hour at least). Cool slightly, add 50 ml water and boil for few minutes.

##### 4.2 Gravimetric Quinoline, Molybdate method for determination of total phosphorus.

##### Reagents

1. Citric molybdic acid reagent—Dissolve 54 gm, 100 per cent molybdic anhydride ( $\text{M}_2\text{O}_3$ ) and 12 gm  $\text{NaOH}$  with stirring in 400 ml hot water and cool. Dissolve 60 gm citric acid in mixture of 140 ml  $\text{HCl}$  and 300 ml water and cool. Gradually add molybdic solution to citric acid solution with stirring. Cool, filter and dilute to 1 litre. (Solution may be green or blue, colour depends on exposure to light). If necessary add 0.5 per cent  $\text{KBrO}_3$  solution drop by drop until green colour becomes pale. Store in dark in polyethylene bottle.



2. Quinoline solution—Dissolve 50 ml synthetic quinoline with stirring in mixture of 60 ml HCl and 30. ml. water. Cool dilute to 1 litre, and filter. Store in polyethylene bottle.

3. Quimociac reagent—Dissolve 70 gm of sodium molybdate dihydrate in 150 ml water. Dissolve 60 gm citric acid in mixture of 85 ml  $\text{HNO}_3$  and 150 ml water and cool. Gradually add molybdate solution to citric acid-nitric acid mixture with stirring. Dissolve 5 ml synthetic quinoline in mixture of 35 ml  $\text{HNO}_3$  and 100 ml water. Gradually add this solution to molybdate citric-nitric acid solution mix and let it stand for 24 hours. Filter, add, 28 ml acetone, dilute to 1 litre with water and mix well. Store in polyethylene bottle.

#### Procedure

1. Treat 1 gm sample as prescribed in 4.1 and dilute it to 200 ml.

2. Pipette into 500 ml erlenmeyer flask, aliquot containing not more than 25 mg  $\text{P}_2\text{O}_5$ , dilute to approximately 100 ml with water. Proceed with one of the following methods.

(a) Add 30 ml citric molybdic acid reagent and boil gently for 3 minutes. (Solution must be precipitate free at this stage). Remove from heat and swirl carefully. Immediately add from burette 10 ml quinoline solution with continuous swirling. (Add first 3-4 ml dropwise and remainder in steady stream) or

(b) Add 50 ml quimociac reagent, cover with watch glass place on hot plate in well ventilated hood, and boil for 1 minute.

After treatment with (a) or (b) cool to room temperature, swirl carefully 3-4 times during cooling, filter into gooch with glass fibre filter paper previously dried at  $250^\circ\text{C}$  and weighed, and wash five times with 25 ml portion of water. Dry crucible and contents for 30 minutes at  $250^\circ\text{C}$ . Cool in desiccator to constant weight as  $(\text{C}_9\text{H}_7\text{N})_3\text{H}_3\text{PO}_4 \cdot 12 \text{M}_2\text{O}_3$ . Subtract weight reagent blank. Multiply by 0.03207 to obtain weight of  $\text{P}_2\text{O}_5$ . Report as per cent  $\text{P}_2\text{O}_5$ .

#### 4.3 Determination of water soluble phosphorus

##### Procedure

1. Place 1 gm sample on 9 cm filter paper and wash with small portion of water until filtrate measure approximately 250 ml.

2. Let each portion pass through filter before adding more and use suction if washing would not otherwise be complete within 1 hour.

3. If the filtrate is turbid, add 1-2 ml  $\text{HNO}_3$ , dilute to 250 ml and mix.

4. Pipette into 500 ml erlenmeyer flask aliquot containing not more than 25 mg  $\text{P}_2\text{O}_5$ .

5. Dilute if necessary to 50 ml.

6. Add 10 ml  $\text{HNO}_3$  (1 plus 1) and boil gently for 10 minutes. Cool and dilute to 100 ml and proceed as 4.2 (b).

(Reference "Methods of Analysis, AOAC).

#### 4.4 Citrate Insoluble phosphorus.

##### Reagents

1. Ammonium citrate solution—should have specific gravity of 1.09 at  $20^\circ\text{C}$  and pH of 7.0 as determined electrometrically.

Dissolve 370 gm crystalline citric acid in 1.5 litre distilled water and nearly neutralize by adding 345 ml  $\text{NH}_4\text{OH}$  (28-29%  $\text{NH}_3$ ). If concentration of ammonia is less than 28 per cent add correspondingly larger volume, and dissolve citric acid in correspondingly smaller volume of water. Cool and check pH. Adjust with  $\text{NH}_4\text{OH}$  (1 plus 7) or citric acid solution to pH 7. Dilute solution if necessary to specific gravity of 1.09 at  $20^\circ\text{C}$ . (Volume will be approximately 2 litres). Keep in tightly stoppered bottles and check pH from time to time. If pH has changed from 7.0, readjust.

2. Other reagents and solutions as in 4.1 and 4.2.

##### Procedure (Acidulated samples and mixed fertilisers).

1. After removing water soluble  $\text{P}_2\text{O}_5$  in 4.3 transfer filter and residue within 1 hour to 200 or 250 ml flask containing 100 ml ammonium acetate solution previously heated to  $65^\circ\text{C}$ .

2. Close flask tightly with smooth rubber stopper.

3. Shake vigorously until paper is reduced to pulp and relieve pressure by removing stopper momentarily.

4. Continuously agitate contents of stopper flask in apparatus equipped to hold contents of flask at exactly 65°C. (Action of apparatus should be such that dispersion of sample in citrate solution is continually maintained and entire inner surface of flask and stopper is continually bathed with solution).

5. Exactly 1 hour after adding filter and residue, remove flask from apparatus, and immediately filter contents by suction as rapidly as possible through whatman No. 5 paper or equivalent, using buchner or ordinary funnel with platinum or other cone.

6. Wash with distilled water and at 65°C until volume of filtrate is approximately 350 ml, allowing time for thorough draining before adding more water.

7. If material is one that will yield cloudy filtrate, wash with 2 per cent  $\text{NH}_4\text{NO}_3$  solution.

8. Determine  $\text{P}_2\text{O}_5$  in citrate insoluble residue by one of the following methods:

(1) Dry paper and contents, transfer to crucible, ignite until all organic matter is destroyed, and digest with 10-15 ml HCl until all phosphate dissolve, or (2) treat wet filter and contents as in method prescribed in 4.1 (a), (c), (d) or (e). Dilute solution to 250 ml or other suitable volume, mix well filter through dry paper and determine  $\text{P}_2\text{O}_5$  as in 4.2.

(Reference "Methods of Analysis" AOAC, 1965).

#### 4.5 Citrate soluble phosphorus

Subtract sum of water soluble and citrate insoluble  $\text{P}_2\text{O}_5$  from total  $\text{P}_2\text{O}_5$  to obtain citrate soluble  $\text{P}_2\text{O}_5$ .

(Reference "Methods of Analysis" AOAC, 1965).

#### 4.6 Citric acid soluble $\text{P}_2\text{O}_5$ in fertilisers other than basic slag

##### Reagents

1. Concentrated hydrochloric acid
2. Concentrated nitric acid
3. Calcium oxide finely ground
4. 5 N Sodium hydroxide solution.
5. Dilute hydrochloric acid—Dilute 240 ml of concentrated hydrochloric acid with water to 1 litre.
6. Citric molybdic acid solution—Stir 54 gm of molybdic anhydride ( $\text{MOO}_3$ ) with 200 ml of water, add 11 gm of sodium hydroxide and stir the mixture whilst heating to boiling point until the molybdic anhydride dissolves. Dissolve 60 gm of citric acid in about 250 to 300 ml of water and add 140 ml of concentrated hydrochloric acid. Pour the molybdate solution into the acid solution, which is stirred throughout the addition. Then cool and if necessary filter the solution through paper pulp pad. Dilute the solution to 1 litre. If the solution is slightly green or blue in colour add dropwise a dilute (0.5 to 1.0 per cent) solution of potassium bromate until the colour is discharged. This reagent should be kept in dark.
7. Quinoline solution—Measure 60 ml of concentrated hydrochloric acid and 300 to 400 ml of water into a 1 litre beaker and warm to 70°–80°C. Pour 50 ml of quinoline in a thin stream into the dilute acid whilst stirring. When quinoline has dissolved, cool the solution dilute to 1 litre, and if necessary filter through a paper pulp filter.
8. Sodium hydroxide solution—0.5 N carbonate free.
9. Indicator solution—Mix three volumes of thymol blue solution and two volumes of phenolphthalein solution prepared as follows:
  - (a) Thymol blue solution—Dissolve 250 mg thymol blue in 5.5 ml of 0.1 N sodium hydroxide solution and 125 ml of industrial methylated spirit. Dilute with water to 250 ml.
  - (b) Phenolphthalein solution—Dissolve 250 mg phenolphthalein in 150 ml of industrial methylated spirit and dilute with water to 250 ml.
10. Hydrochloric acid—0.5 N.

11. Sodium hydroxide solution—0.1 N.

12. Hydrochloric acid—0.1 N.

13. Surface active agent—0.5 per cent solution of sodium dodecyl benzene sulphonate: as suitable.

**Preparation of solution**

1. Weight to the nearest mg about 5 gm of the sample and transfer to a stoppered bottle of about 1 litre capacity.
2. Dissolve 10 gm of pure crystallized citric acid (monohydrate) in water, dilute to 500 ml and adjust the temperature to 20°C.
3. Add the solution to the sample in the bottle, shaking so as to avoid the possibility of caking.
4. Shake the bottle continuously for 30 minutes.
5. Pour the whole of the liquid at once on to a large medium-fine filter and collect the filtrate. If the filtrate is not clear, pass it again through the same filter.

**Procedure**

1. Transfer a volume of the solution prepared according to procedure given above containing less than 70 mg of phosphoric acid and preferably about 50 mg to a 500 ml stoppered conical flask marked at 150 ml.
2. Dilute the solution with water to 100 ml.
3. If the sample does not contain calcium add 100 to 200 mg of calcium carbonate.
4. Then add 5 N sodium hydroxide solution dropwise until a faint permanent turbidity or precipitate is formed.
5. Dissolve the precipitate by the dropwise addition of dilute hydrochloric acid, but avoid an excess.
6. Dilute to 150 ml and add 50 ml of the citric-molybdic acid reagent, and heat the solution to incipient ebullition, maintain it at this temperature for 3 minutes and then bring it to the boiling point.
7. From burette slowly add 25 ml of the quinoline solution with constant swirling throughout the first few ml, being added dropwise, the rest in a slow stream.
8. Keep the solution gently boiling during the addition.
9. Immerse the flask in boiling water for 5 minutes, then cool it to 15°C in running water.
10. Filter with suction the contents of the flask on a paper pulp pad, and wash the flask precipitate and filter with successive small washes of cold water until they are free from acid.
11. Transfer the filter pad and precipitate to the original flask, rinse the funnel with water, and collect the rinsings in the flask.
12. If necessary, wipe the funnel with small piece of damp filter paper to ensure complete removal of the precipitate, and place the paper in the flask.
13. Add water to a total of about but not exceeding 100 ml. Stopper the flask and shake it vigorously until the pulp and precipitate are completely dispersed.
14. Remove the stopper and wash it with water, returning the washings of the flask.
15. Add a measured volume of 0.5 N sodium hydroxide solution sufficient to dissolve the precipitate and leave a few ml in excess.
16. Shake the flask vigorously until all the precipitate dissolves. (To facilitate the dispersal of the precipitate, after the addition of 0.5 N sodium hydroxide solution, a few drops of the surface active agent may be added if necessary).
17. Add 0.5—1.0 ml of the indicator solution, and titrate the excess of sodium hydroxide with 0.5 N hydrochloric acid, until the indicator changes from violet to green-blue, and then very sharply to yellow at the end point.

18. Deduct the number of ml of 0.5 N hydrochloric acid used from the number of ml 0.5 N sodium hydroxide, to ascertain the volume of 0.5 N sodium hydroxide equivalent to the phosphoric acid.

19. Carry out a blank determination on all the reagents, omitting only the sample, and using 0.1 N standard alkali and acid instead of 0.5 N for the titration. Calculate the blank in terms of 0.5 N alkali and subtract it from the original result.

20. Calculate the amount of phosphoric acid in the portion taken for analysis from the factor 1.0 ml of 0.5 N sodium hydroxide = 1.366 mg  $P_2O_5$ .

(Reference Statutory Instruments 1960, No. 1165, Agriculture, the fertilizer and feeding stuffs Regulations, 1960).

#### 4.7 Free Phosphoric acid (as $P_2O_5$ )

##### Reagents

1. Acetone—conforming to IS : 170-1950 specification for acetone.
2. Standard sodium hydroxide solution—0.1 N
3. Bromocresol green indicator solution—Dissolve 0.1 grms of bromocresol green in 100 ml. of rectified spirit conforming to IS : 323-1959 specification for rectified spirit (Revised).

##### Procedure

1. Weigh accurately about 2.5 grms. of the prepared sample and transfer to a Soxhlet extractor.
2. Add about 100 ml of acetone and extract for three hours.
3. Cool and distil off the acetone as far as possible.
4. Take up the residue with water and make up the volume to 250 ml
5. Pipette out exactly 100 ml of this solution and titrate with standard sodium hydroxide solution, using bromocresol green as indicator, until colour just changes from yellow to blue.

##### Calculations

Free phosphoric acid (as  $P_2O_5$ )

$$\text{Per cent by weight} = \frac{17.75 \times V \times N}{W}$$

V=volume in ml of standard sodium hydroxide solution used.

N=normality of standard sodium hydroxide solution, and

W=weight in grms. of sample taken for the test.

[Reference IS specification for superphosphate (Revised) ISI : 294-1962]

#### 5. Determination of Potassium

Determination of Potassium in all kinds of fertilizers is given in this section. Two alternative methods have been described. Any of these two methods may be used depending upon the availability of reagents, and suitability of the method.

##### 5.1 Perchloric Acid method

(This method depends on the insolubility of potassium perchlorate and the solubility of sodium perchlorate in alcohol, and is applicable in presence of alkali metals, chlorides and nitrates. Sulphates and ammonium salts must be absent on account of the low solubility of sodium sulphate and of ammonium perchlorate in alcohol. Phosphates must be removed. Methods are given for the elimination of the effect of interfering substances.)

##### Reagents

1. Concentrated hydrochloric acid.
2. Barium chloride solution—Dissolve 100 grms. of barium chloride in water, filter solution and dilute to 1 litre.

3. Dilute hydrochloric acid—Dilute 240 ml. of concentrated hydrochloric acid with water to 1 litre.
4. Calcium oxide—Finely ground.
5. Ammonium hydroxide solution—sp. gr. 0.88
6. Ammonium carbonate solution—Saturated aqueous solution.
7. Ammonium oxalate solution—Saturated aqueous solution.
8. 20 per cent perchloric acid solution.
9. Alcohol—industrial methylated spirit 95-96 per cent V/V.

10. Wash solution—Add potassium perchlorate to alcohol and shake until a saturated solution is obtained. Keep the solution over solid potassium perchlorate and filter immediately before use.

*Potassium salts free from sulphates and other interfering substances.*

1. Dissolve in water a portion of the sample weighed to the nearest mg. equivalent to potassium content to 1.5 to 2.0 grms. of potash.
2. Cool the solution to 20°C., dilute to 500 ml. in a volumetric flask, mix well and filter through a dry filter.
3. Determine the potash in the 50 ml of solution by precipitating with perchloric acid as described under procedure.

*Potassium salts with sulphates or other interfering substances*

(The following method is given for eliminating the interference caused by presence of sulphate. If salts contain, phosphates, iron, manganese or substances other than sulphate that interfere with the determination of potash, the method described for mixed fertilizer should be used).

1. Weigh to the nearest mg a portion of the sample equivalent in potassium content to 1.5 to 2.0 gm of potash, into a 500 ml. beaker. Add about 300 ml of water and 20 ml concentrated hydrochloric acid and heat the solution to boiling.
2. To the boiling solution cautiously, add drop by drop, barium chloride solution in an amount slightly in excess of that previously determined as necessary to ensure the complete precipitation of sulphate.
3. Cool the liquid to 20°C, transfer to a 500 ml. volumetric flask, dilute to 500 ml., mix and filter through a dry filter.
4. Take 50 ml of the filtrate and evaporate to dryness in a basin, moisten the residue with concentrated hydrochloric acid.
5. Again evaporate to dryness, dissolve the residue with 5-10 ml. dilute hydrochloric acid and filter if necessary. Determine the potash in the solution by the method described under procedure.

*Potassium in mixed fertilizers*

1. Weigh to the nearest centigram about 10 gm. of the sample and if organic matter is present, gently incinerate at a temperature not exceeding 500°C.
2. Transfer the weighed portion of the sample or the incinerated residue to a 500 ml. beaker with a little water and 10 ml. concentrated hydrochloric acid and then warm for 10 minutes.
3. Dilute with water to about 300 ml. and bring gradually to boiling point.
4. Add 10 gm of calcium oxide made into a paste with water.
5. Bring contents again gently to the boiling point, and keep so heated for about half an hour with frequent stirring.
6. Cool to 20°C., transfer to a 500 ml. volumetric flask, dilute to 500 ml. and, after thoroughly shaking filter through a dry filter paper.
7. Transfer 250 ml. of the filtrate to another 500 ml. volumetric flask, make just acid with hydrochloric acid and heat to boiling point.

8. To the boiling solution cautiously add drop by drop, barium chloride solution until there is no further precipitation of barium sulphate.
9. Render the contents of the flask alkaline with ammonium hydroxide solution, and precipitate the calcium and any excess of barium by adding of ammonium carbonate solution until no further visible precipitation occurs followed by the addition of about 1 ml of ammonium oxalate solution.
10. Cool to 20°C, dilute with water to 500 ml and, after thoroughly shaking, filter through a dry filter paper.
11. Measure 100 ml. of the filtrate and evaporate to dryness in a basin. Expel the ammonium salts from the residue by gently heating the basin over a low flame, being careful to keep the temperature below that of faint redness.
12. Cool the residue, moisten with concentrated hydrochloric acid and again evaporate to dryness.
13. Take up the residue with water and filter if necessary.
14. Determine the potash in the solution by precipitation with perchloric acid as described under procedure.

#### *Procedure*

1. Transfer the solution obtained as described above into a basin and add about 7 ml of perchloric acid solution.
2. Place the basin on a hot plate or sand bath and evaporate the contents until the white fumes are copiously evolved.
3. Cool and dissolve the precipitate in a little hot water.
4. Add about 1 ml of perchloric acid solution and again concentrate to the fuming stage.
5. Thoroughly cool the residue in the basin and stir in 20 ml of alcohol.
6. Allow the precipitate to cool and settle, then pour the clear liquid through a dry filter paper, draining the precipitate in the basin and stir in 20 ml of alcohol.
7. Allow the precipitate to cool and settle, then pour the clear liquid through a dry filter paper, drain the precipitate in the basin as completely as possible.
8. Redissolve the precipitate on the paper and that remaining in the basin with hot water.
9. Add 2 ml of perchloric acid solution to the combined solution and evaporate the whole down to the fuming stage.
10. Cool the residue in the basin and thoroughly stir the contents with 20 ml of alcohol.
11. Allow the precipitate to cool and settle and pour the clear liquid through a weighed good or sintered glass crucible, draining the precipitate as completely as possible from the liquid before adding 5 ml of wash solution.
12. Wash the precipitate by decantation with several similar small portions of the wash solution, pouring the washings through the crucible.
13. Transfer the precipitate to the crucible and wash it well with the wash solution until free from acid.
14. Dry the precipitate at 100° C and weigh.
15. Regard the precipitate as potassium perchlorate ( $\text{KClO}_4$ ) and calculate its equivalent as potash  $\text{K}_2\text{O}$  by multiplying its weight by 0.34.

(Reference statutory Instruments 1960. No. 1165, Agriculture, the fertilizer and Feeding stuffs Regulation 1960).



### 5.2 Sodium Tetraphenylboron Method

This method is applicable to both mixed and straight potassium fertilizers.

#### Reagents

(a) Sodium hydroxide solution—20 per cent. Dissolve 20 gm NaOH in 100 ml distilled water.

(b) Formaldehyde solution—37 per cent.

(c) Sodium tetraphenylboron (STB) Solution—Approximately 1.2 per cent. Dissolve 12 gm sodium tetraphenylboron in approximately 800 ml water. Add 20-25 gm  $\text{Al}(\text{OH})_3$ , stir for 5 minutes, and filter (whatman No. 42 paper or equivalent) into 1 litre volumetric flask. Rinse beaker sparingly with water and add to filter. Collect entire filtrate, add 2 ml 20 per cent NaOH solution, dilute to volume with water, and mix. Let it stand for 48 hours and standardize. Adjust so that 1 ml STPB = 1 per cent  $\text{K}_2\text{O}$ . Store at room temperature.

(d) Quaternary ammonium chloride solution.—

Approximately 0.625 per cent. Dilute 50 ml of 12.8 per cent Zephiran chloride to 1 litre with water, mix and standardize. Cetyltrimethyl—ammonium bromide may be substituted for Zephiran chloride. If other concentration is used, adjust volume.

(e) Clayton yellow—0.04 per cent. Dissolve 40 mg in 100 ml water.

#### Standardization of Solution

(a) Zephiran chloride—To 1.0 ml STB solution in 125 ml erlenmeyer flask, add 20-25 ml water, 1 ml 20 per cent NaOH, 2.5 ml  $\text{HCHO}$ , 1.5 ml 4 per cent  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and 6-8 drops of indicator(e).

(b) Titrate to pink and point with Zephiran chloride solution, using 10 ml semimicro buret. Adjust Zephiran chloride solution so that 2.0 ml = 1.0 ml STPB solution.

(c) Sodium tetraphenyl boron solution—Dissolve 2.5 gm of  $\text{KH}_2\text{PO}_4$  in water in 250 ml volumetric flask, add 50 ml 4 per cent  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution, dilute to volume with water and mix. (It is not necessary to bring to boil). Transfer 15 ml aliquot (51.92 mg  $\text{K}_2\text{O}$ , 43.10 mg K) to 100 ml volumetric flask, add 2 ml 20 per cent NaOH, 5 ml  $\text{HCHO}$  and 43 ml STPB reagent. Dilute to volume with water, mix thoroughly, let stand 5.10 minutes and pass through dry filter. Transfer 50 ml aliquot of filtrate to 125 ml erlenmeyer flask, add 6-8 drops of indicator(e) and titrate excess reagent with Zephiran solution. Calculate titratic value as follows :

$$F = 34.61 / (43 \text{ ml} - \text{ml Zephiran}) = \% \text{ K}_2\text{O} / \text{ml STPB reagent.}$$
 Factor applies to all fertilizers if 2.5 gm sample is diluted to 250 ml. and 15 ml aliquot is taken for analysis. If results are to be expressed as K rather than  $\text{K}_2\text{O}$ , substitute 28.73 for 34.61 in calculating the value of F.

#### Preparation of solution

1. Place 2.5 gm. sample or factor weight 2.430 gm in 250 ml. volumetric flask.

2. Add 125 ml water and 50 ml saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution. Add 1 ml of diglycol stearate solution if needed to prevent foaming.

3. Boil for 30 minutes, add slight excess of  $\text{NH}_4\text{OH}$  and after cooling dilute to 250 ml. Mix and pass through dry filter.

(b) Potassium salts (Potassium chloride, sulphate, potassium magnesium sulphate, and kairuit).

1. Dissolve 2.5 gm. or factor weight 2.430 gm and dilute to 250 ml without adding  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .

2. When interfering substances such as  $\text{NH}_3$ , Ca, Al etc. are present, proceed as in (a).

*Procedure*

1. Transfer 15 ml aliquot of sample solution to 100 ml volumetric flask and add 2 ml. 20 per cent NaOH and 5 ml HCHO.
2. Add 1 ml standard STPB solution for each 1 per cent  $K_2O$  expected in sample plus additional 8 ml excess to insure complete precipitation.
3. Dilute to volume with water, mix thoroughly let it stand for 5-10 minutes and pass it through dry filter (whatman 12 or equivalent).
4. Transfer 50 ml filtrate to 125 ml erlenmeyer flask, add 6-8 drops of indicator(e) and titrate excess reagent with standard Zephiran Solution.

$$\%K_2O \text{ in the sample} = (\text{ml STPB added} - \text{ml Zephiran}) \times F,$$

where  $F = \%K_2O/\text{ml, STPB reagent.}$

(Reference "Methods of Analysis", AOAC, 1965.)

- (10) In the said Order, in Form 'A', for Note (1) the following Note shall be substituted namely :—

NOTE : (i) Where the business of selling fertilisers is carried on at more than one place a separate application should be made for registration in respect of each such place.

- (11) In the said Order, for Form 'B', the following Form shall be substituted, namely:

## EMBLEM

## FORM 'B'

(See clause 7)

Block No. ....

Registration No. ....  
Date of Issue .....  
Valid upto .....

Certificate of Registration to carry on the Business of Dealer in Fertilisers in the State of, ..... is hereby granted certificate of registration to carry on the business of selling fertilisers at the place prescribed below in the State subject to the terms and conditions specified below and to the provisions of the Fertiliser (Control) Order, 1957.

*Description of the place of business*

Name or style by which the business is carried on Location of sale depot

Location of godowns attached to sale depot

Date :

Registering Authority

State of .....

Seal



*Terms and conditions of certificate of registration*

1. This certificate of registration shall be displayed in a prominent and conspicuous place in a part of the business premises open to the public.
2. The holder of the certificate shall comply with the provisions of the Fertiliser (Control) Order, 1957 and the notifications issued thereunder for the time being in force.
3. The certificate of registration shall come into force immediately and be valid upto the 31st March, 19.....unless previously cancelled or suspended.
4. The holder of the certificate shall from time to time report to the Registering Authority any change in the premises where he carries on his business of selling fertilisers.
5. The dealer shall submit a report to the Registering Authority, with a copy to the Block Development Officer or such officer as the State Government may notify in whose jurisdiction the place of business is situated, by the 5th of every month, showing the opening stock, receipts, sale and closing stocks of fertilisers in the preceding month. He shall also submit in time such other returns as may be prescribed by the Registering Authority.
6. The dealer transacting retail sales shall keep in stock for sale fertilisers having nitrogenous phosphatic ( $P_2O_5$ ) and potash nutrients separately or jointly, provided that the nutrient stock of phosphate ( $P_2O_5$ ) and potash ( $K_2O$ ) together shall not be less than 20% of the nitrogen in stock.

NOTE : (1) Where the business of selling fertilisers is carried on at more than one place a separate registration certificate should be obtained in respect of each place.

- (12) After Form 'EE' of the said Order, the following forms shall be inserted, namely:—

## EMBLEM

## FORM 'F'

[See Clause 13 (B)]

Application for grant of permission to sell non-standard fertilisers

To

The Registering Authority  
State of .....

1. Full name and address of the applicant.
2. The name of fertilisers in which the applicant has been authorised to carry on business.
3. Number and date of registration certificate granted in favour of the applicant.
4. The particulars of non-standard fertilisers which are intended to be sold:
  - (i) Name of the fertiliser.
  - (ii) The source from which the fertilisers were originally purchased and the period during which they have been held by the applicant. Brief reasons leading to the material having become non-standard.
  - (iii) The chemical specifications as analysed by an authorised chemical laboratory.
  - (iv) Name and appearance of the non-standard fertiliser.

NOTE : Chemical analysis to be indicated shall be one which has been certified by an authorised chemical laboratory on the basis of the samples drawn, sealed and despatched in the presence of the local Inspector of Fertilisers or anybody authorised to inspect the fertilisers.

I enclose a copy of the certificate of registration for dealing in fertilisers already granted to me and I have deposited the prescribed fee for permission to sell non-standard fertilisers.

I certify that I will comply with the requirements of sub-clause(a) of Clause 13(B) of the Fertiliser Control Order, 1957 which requires that each container of non-standard fertilisers is to be conspicuously superscribed with the words 'Non-Standard' and also with the sign "X", both in red colour.

Signature of the applicant,

## EMBLEM

FORM 'G'  
[See Clause 13(B)]

Book No. ....

Date of issue :

Valid upto .....  
(the period of validity will not  
exceed 4 months from the date  
of issue).

*Permission for the sale of non-standard fertilisers*

M/s. .... is/are hereby permitted to sell the non-standard  
fertilisers described below subject to the terms and conditions noted hereunder :—

*Particulars of non-standard fertiliser*

1. Name of the fertiliser
2. Detailed chemical specifications including the nutrient content.
3. Nature and appearance of the non-standard fertiliser.
4. Place of location of the non-standard fertiliser.

*Terms and conditions*

1. The seller of the non-standard fertiliser as described above shall comply with the provisions of sub-clause(a) of Clause 13(B) of the Fertiliser Control Order, 1957.

2. The non-standard fertilisers as described above shall be sold at a price not exceeding ..  
.....per metric tonne or.....per bag of.....kgs.

3. If the non-standard material described above is not sold before..... a fresh permission will be necessary before the non-standard fertiliser can be sold.

Date

Registration Authority

Seal

State of.....

[No. 16/17/68-M.]

S. M. H. BURNEY, Jt. Secy.